

ASSESSING THE POTENTIAL OF DISINFECTION BYPRODUCTS IN DRINKING
WATER FROM GROUNDWATER IN NORTH CAROLINA AQUIFERS

By

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29 April 2016

Masters project submitted in partial fulfillment of the
requirements for the Master of Environmental Management degree in
the Nicholas School of the Environment of
Duke University

Executive Summary

Over half of the global population lives within 200 kilometers of a coastline. Many communities rely heavily on groundwater from coastal aquifers, which have distinct geochemical compositions based on geologic history, hydrogeology, and geographic positioning. Due to the proximity of these aquifers to seawater, they may have increased concentrations of halide ions including chloride, bromide, and iodide. Halides are important to quantify in drinking water because of their role in the formation of byproducts during drinking water disinfection.

In the United States, approximately 80% of drinking water is disinfected with chlorine. Halide ions have been relatively recently discovered to be precursors of disinfection byproducts (DBPs), some of which are classified as possible human carcinogens. The US Environmental Protection Agency (EPA) regulates four trihalomethanes (listed as Total Trihalomethanes or TTHM), with the main focus on chloride-induced DBP formation. However, recent studies have shown that bromide and iodide, although typically found in significantly lower concentrations, have the chemical potential to produce a higher amount of more toxic DBPs than those currently being regulated. Dissolved organic carbon (DOC) is another precursor, and although not well researched due to its unpredictable and variable structure, has still been proven to produce dangerous DBPs as well. Chloride is the only halide regulated by the EPA with a Maximum Contaminant Level (MCL) of 250 mg/L. Even though most public utilities meet this standard, many still see an elevated TTHM concentration, meaning other factors may be influencing DBP formation.

Our research goal was to quantify the geochemistry of various aquifers near the coast of North Carolina and to establish a correlation of an expanded number of halide concentrations, DOC concentrations, and DBP formation. We collected samples from wells in variable aquifers from nine public utilities along the coast, with each utility serving a relatively large population, using chlorination for disinfection, and reporting elevated TTHMs. We analyzed these for halide ion concentrations and DOC concentrations. Samples were also sent to Stanford University, where a lab ran a simulation analysis to quantify amounts of a range of regulated and unregulated DBPs that formed when the raw groundwater samples were chlorinated.

Our findings show that the ratio of chloride and bromide concentrations found in our samples resembles that of groundwater experiencing seawater intrusion. The formation of DBPs quantified in our analysis is significantly correlated with levels of bromide, iodide, DOC, and

electrical conductivity. Additionally, use of chloramines to disinfect the water resulted in significant reductions in TTHMs, and one of the major factors in formation, bromide, can also be significantly reduced with the usage of ion filtration systems such as reverse osmosis. These two methods could be potential options to reduce DBPs, by removing the constituents which contribute to their formation. Given the statistically significant correlation between TTHMs formed from drinking water disinfection and the levels of DOC and conductivity, we postulate that this could be a relatively inexpensive method of characterizing potential DBP formation in water prior to treatment, and could lead to the implementation of advance measures to reduce amounts of these compounds entering drinking water treatment systems.

Stresses such as over pumping, sea level rise, and seawater intrusion are viable threats to altering the geochemistry of coastal aquifers, with in increased risk of elevating these concentrations of halides. Identifying and understanding each factor and its role in DBP formation is necessary to monitor, prevent, and mitigate any changes to the drinking water supply as it relates to public health presently and in the future.

Table of Contents

Executive Summary	2
Introduction	5
<i>The Coastal Plain</i>	5
<i>Geology</i>	6
<i>Hydrogeology</i>	7
<i>Disinfection Chemistry and Byproduct Formation</i>	9
<i>Disinfection Regulation</i>	11
Materials and Methods	12
<i>DBP Simulation Methodology</i>	16
Results and Discussion	17
<i>Geospatial Analysis</i>	18
<i>Statistical Analysis</i>	29
<i>Implications</i>	36
<i>Source Water and Monitoring Samples</i>	43
<i>Solutions to reduce DBP formation in Drinking Water</i>	48
<i>Uncertainties</i>	49
Conclusion	50
Acknowledgements	51
References	52
Appendices	
<i>A: Raw data tables</i>	55
<i>B: Raw data tables of previously collected samples within Dare County Water System</i>	63
<i>C: USGS Castle Hayne and Peedee Data</i>	68
<i>D: R code for statistical analyses</i>	70
<i>E: Geospatial Methodology and Python Script</i>	75

Introduction

Over half of the world's population lives within 200 km of a coastline, and more than one billion people globally rely on coastal aquifers as a water source¹. The population in U.S. coastline counties has grown steadily in recent years, with the Atlantic coastline region experiencing the largest gains since 1990². In North Carolina, approximately 1.5 million people are supplied community water from coastal groundwater aquifers³. This research characterizes the chemical composition of groundwater between several aquifers in the North Carolina Coastal Plain and clarifies the factors that affect the relationship between geochemistry and disinfection byproduct (DBP) formation. By researching public drinking water utilities use groundwater, sampling source and treated water, characterizing the geochemistry of the aquifers, and simulating disinfection to quantify DBP formation, we can better identify the causes of elevated DBP occurrence throughout the North Carolina Coastal Plain and use these results as a tool for predicting DBP formation in coastal communities.

Coastal Plain

The Coastal Plain of North Carolina is part of the Atlantic and Gulf Coastal Plain physiographic province of the United States, which extends from Cape Cod, Massachusetts south and west into Texas. In North Carolina, the Coastal Plain is roughly 90-150 miles wide from the Atlantic Ocean west to the Fall Line. It is comprised of the eastern 41 counties and makes up about 45% of the state's total land area, as shown in Figure 1 below⁴. The Fall Line characterizes the boundary between the crystalline basement rocks of the Piedmont and the sedimentary rocks of the Coastal Plain. We chose the Coastal Plain as our research area because many communities within this region use groundwater as a primary drinking water source, and with close proximity to the ocean and the geologic history, salinity of drinking water is already a concern for utilities.

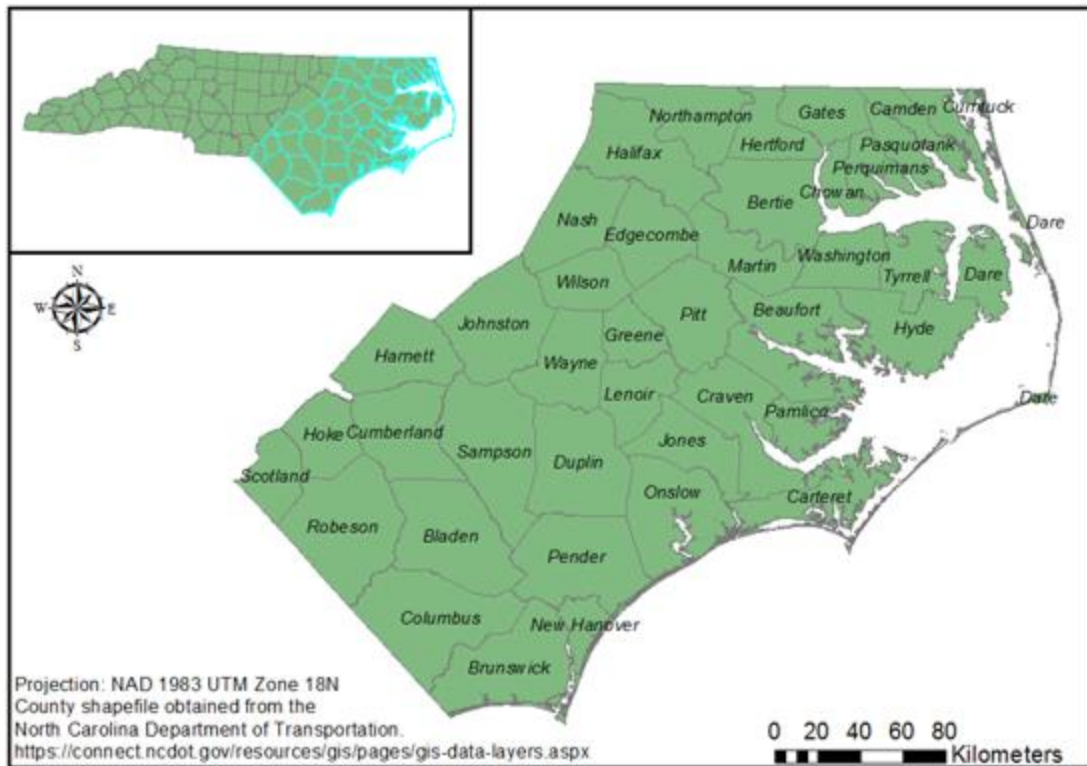


Figure 1: North Carolina Coastal Plain Counties.

Geology

The regional structure of sedimentary rocks of the Coastal Plain area is a broad eastward-dipping monocline, shown in Figure 2, which plunges southeastward⁵. Underlying the sediments of the Coastal Plain are crystalline Precambrian rocks of the Piedmont physiographic province. The Coastal Plain sediments were deposited under nonmarine and marginal marine conditions throughout the transgression and regression of the Atlantic Ocean⁶. Sediments dip and thicken eastward from the Fall Line, spanning from the Lower Cretaceous to the Quaternary in age⁷. Our focus encompasses the geologic units which comprise the selected aquifers of our study.

Beginning with the oldest formation, The Lower Cape Fear aquifer is composed of older sand beds of the Cape Fear formation⁶. In this formation, our main focus is the Upper Cape Fear aquifer, which comprises the permeable zones in the Cape Fear formation and is the lowest member in the Peedee-Upper Cape Fear aquifer system. The Upper Cape Fear consists of alternating beds of fine-to-medium grained quartz sand and clay that are commonly 3-5 feet thick but can attain a thickness of fraction of a foot to over 15 feet⁷.

The Black Creek aquifer consists mainly of sediments of both Black Creek and Middendorf formations of the Late Cretaceous age⁶. The Black Creek formation was deposited in lagoonal and marine environments, and consists of thinly laminated gray to black clay interlayered with gray-to-tan lignitic, glauconitic, and shelly sands¹⁰. The Middendorf formation is composed of a heterogeneous mix of fine- to medium- grained sand and silty clay beds, coarse channel sand, and thin laminated beds of sand and clay, all of nonmarine origin. Beds can be white, tan, and red in color, and often contains kaolinite fragments⁶. The Black Creek aquifer is the thickest and most productive in the Peedee-Upper Cape Fear aquifer system⁷.

The Peedee aquifer is comprised largely of the Late Cretaceous age Peedee formation and contains of fine- to medium- grained quartz sand interbedded with gray-to-black marine clay and silt⁷. Sand beds are commonly gray or greenish-gray and contain varying amounts of glauconite and shell material¹⁰. It is the youngest member of the Peedee-Upper Cape Fear aquifer system.

The Castle Hayne aquifer includes sediment from the Pungo River Miocene, the upper part of the Paleocene Beaufort formation⁹, and the Eocene Castle Hayne limestone with rocks overlying of Oligocene-age clay. The units were deposited under marine conditions, and are composed predominantly of limestone and sandy marl¹⁰, with trace amounts of clay. Shells, limestone, and sandy limestones, in addition to the sand beds are variable in their carbonate content. Geophysical logs show increasing silt and clay content near the bottom of the aquifer. Along its western margin from New Hanover County to Craven County, the Castle Hayne can be found near land surface and exposed in many streams, but it does not extend to the western or southwestern margins of the Coastal Plain⁷. As it dips eastward, the aquifer thickens considerably, to more than 950 feet thick in Carteret County⁶. Due to this high volume, the Castle Hayne is the most productive aquifer in North Carolina, with over 65 million gallons being pumped daily for industry alone⁶.

The Yorktown aquifer is generally equated with the Pliocene Yorktown and the upper Miocene Eastover formations. It extends throughout the northern half of the North Carolina Coastal Plain from the Fall Line eastward to and beyond the coast. The aquifer thickens eastward, and although not present in most of the southern half of the Coastal Plain, attains a thickness of more than 300 feet in Dare County⁶. It is composed largely of fine sand, silty and clayey sand, and clay and carbonate shell material, with sediments deposited in marine and near-marine environments⁶.

Evaluating the geology and hydrogeology of our research area is essential to the understanding of the origin and presence of potential geochemical constituents in the groundwater. By using this information in concert with disinfection chemistry, we can better explain DBP formation potential in groundwater throughout the region.

Disinfection Chemistry and Byproduct Formation

Disinfection of drinking water occurs when utilities add chlorine (or a similar oxidant) to source water in order to inactivate pathogens for potable use. This process has played a critical role in improving drinking water quality in the United States since its first application in 1908. Soon after, most of the U.S. began routine disinfection of community drinking water¹¹. Increase in disinfection contributed a dramatic decrease in waterborne disease across the country, particularly cholera, typhoid and dysentery. The successful implementation of disinfection methods for public drinking water is considered one of the greatest public health achievements of the 20th century¹¹.

Two primary methods to control biological growth and remove color, taste, and odor compounds in the U.S. are chlorination and chloramination. 80% of utilities nationwide disinfect via chlorination, which is the process of adding chlorine, a strong oxidant¹². Chlorine is available as compressed elemental gas, sodium hypochlorite solution (NaOCl) or solid calcium hypochlorite (Ca(OCl)₂)¹². The remaining 20% of utilities disinfect via chloramination, which uses a group of compounds containing chlorine and ammonia to disinfect water. Monochloramine (NH₂Cl) is typically used in this method¹³.

Currently, chlorination is a more popular disinfection method than chloramination for several reasons. Chlorine has a longer residual time in water distribution systems, which increases the probability of pathogen inactivation throughout the distribution system¹². In

grow. Recent studies have demonstrated that many nonregulated DBPs are more cytotoxic and genotoxic than the currently regulated THMs and HAAs¹⁵. One study concluded that N-containing DBPs are more toxic than halogenated carbonaceous DBPs and that iodine- and bromine- containing DBPs are more toxic than their chlorinated analogues¹⁷.

Studies which disinfect water samples containing various levels of bromide and iodide have shown that trihalomethane concentrations increase with increasing bromide concentrations, with iodide concentrations leading to the formation of the highest levels of trihalomethanes¹⁸. The maximum concentration was found with iodide concentrations of approximately 2 micromoles/liter, and trihalomethane concentrations decreased when iodide levels increased past that threshold¹⁸. The study also remarks that Total Organic Carbon (TOC) and NOM affect the amount of byproducts formed in extremely complex reaction processes¹⁹. Because bromide and iodide can be found in elevated amounts in coastal aquifers that are in close proximity to seawater or that are at risk for salinization, this potentially poses a large public health risk to coastal communities that rely on disinfected groundwater for drinking.

Materials and Methods

Through a review of North Carolina Coastal Plain drinking water utilities, a dataset was generated of 43 water utilities relying on Coastal Plain aquifers in North Carolina. From this list, a total of nine public utilities were chosen for groundwater sample collection. This was accomplished through the use of a GIS model, shown in Figure 4 which was created to select utilities based on the following criteria:

- Population: In an attempt to quantify the largest effect on population of DBPs in drinking water, utilities that served a population greater than 1,000 were selected, which is shown in Figure 5 on the following page.
- Disinfection method: The primary DBPs focused on in this study are THMs, hence public utilities using only chlorination were kept for consideration. This also maintains an aspect of continuity across utilities and aquifers.

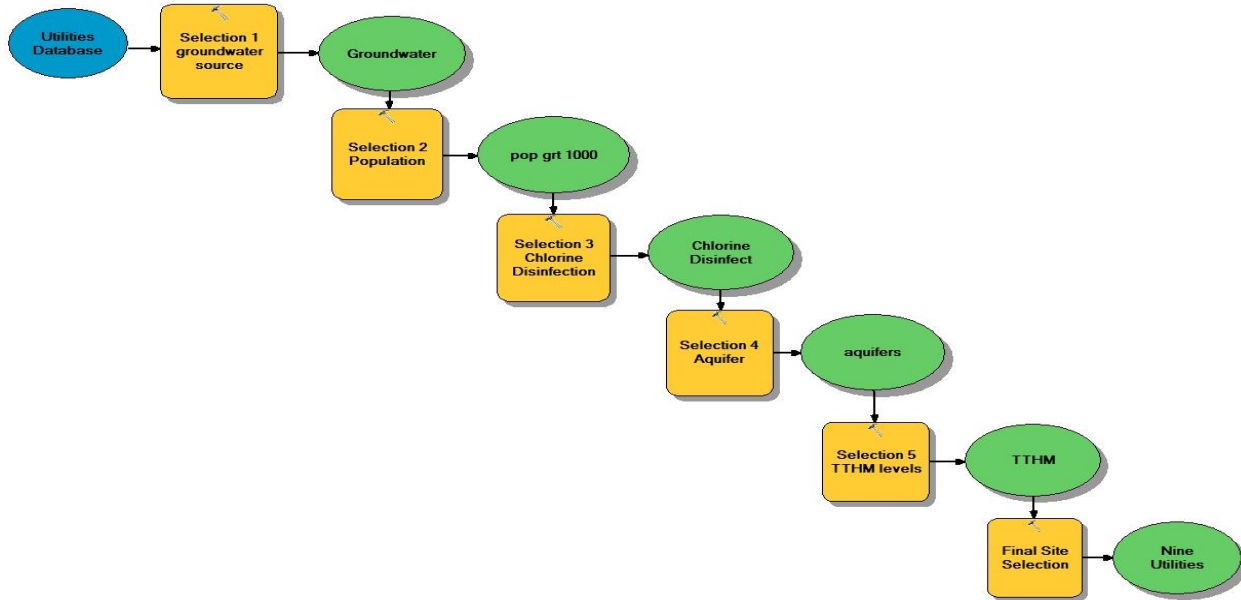


Figure 4: ArcGIS model developed to select of potential utilities to sample based on a set of pre-determined criteria.

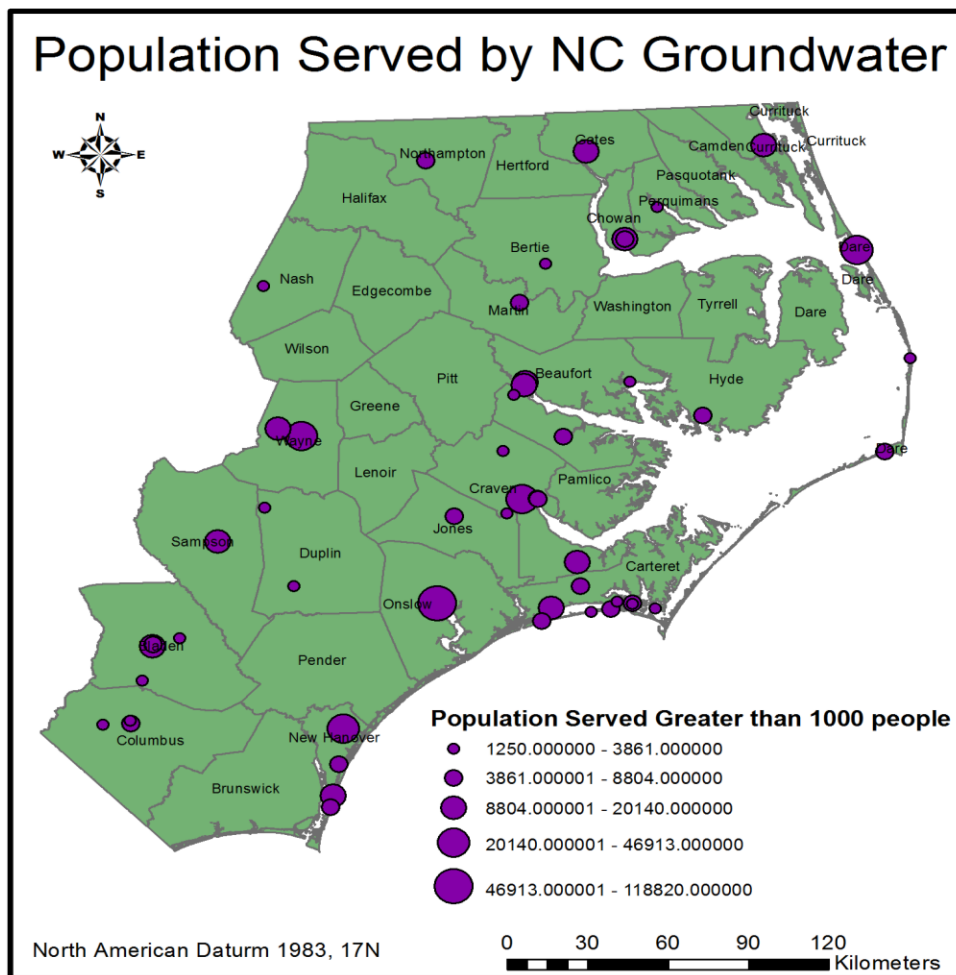


Figure 5: The populations served by the database of drinking water providers in Eastern North Carolina that use groundwater, developed for this research.

- **Aquifer:** A list of utilities was compiled to sample from the various aquifers utilized in NC that maintains an adequate representation of the total use of each aquifer throughout the Coastal Plain. The graph below displays all of the aquifers used by the 43 utilities within the Coastal Plain.

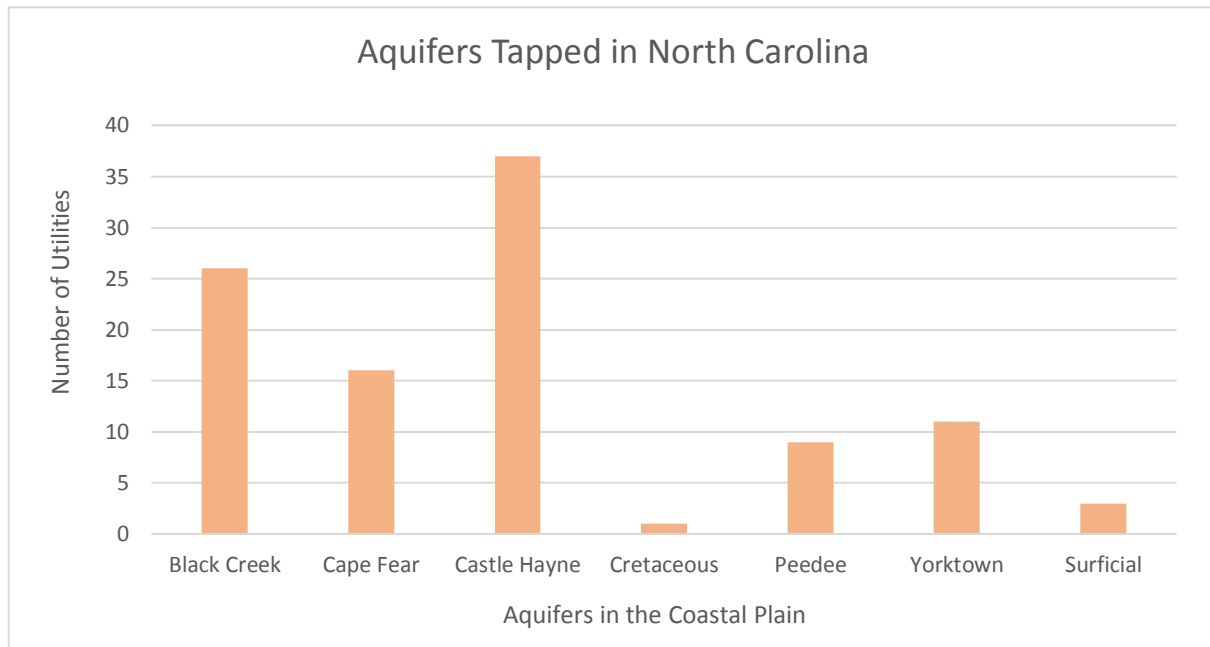


Figure 6: Graph of the usage of seven main aquifers by Eastern North Carolina Drinking Water Utilities. Based on the 43-utility database generated for this sampling collection and research.

- **Trihalomethane concentrations:** The Safe Drinking Water Act (1974) requires community water utilities to publish a Consumer Confidence Report (CCR) each year containing information regarding the water source and levels of detected contaminants. Trihalomethane concentrations from the most recent year available which were considered elevated (at approximately 30 ppb or higher) were the focus for this study. Total trihalomethane (TTHM) concentrations, recorded in utility water quality reports are provided in Figure 7 on the following page. The ArcGIS python script and further methodology are provided in Appendix E.

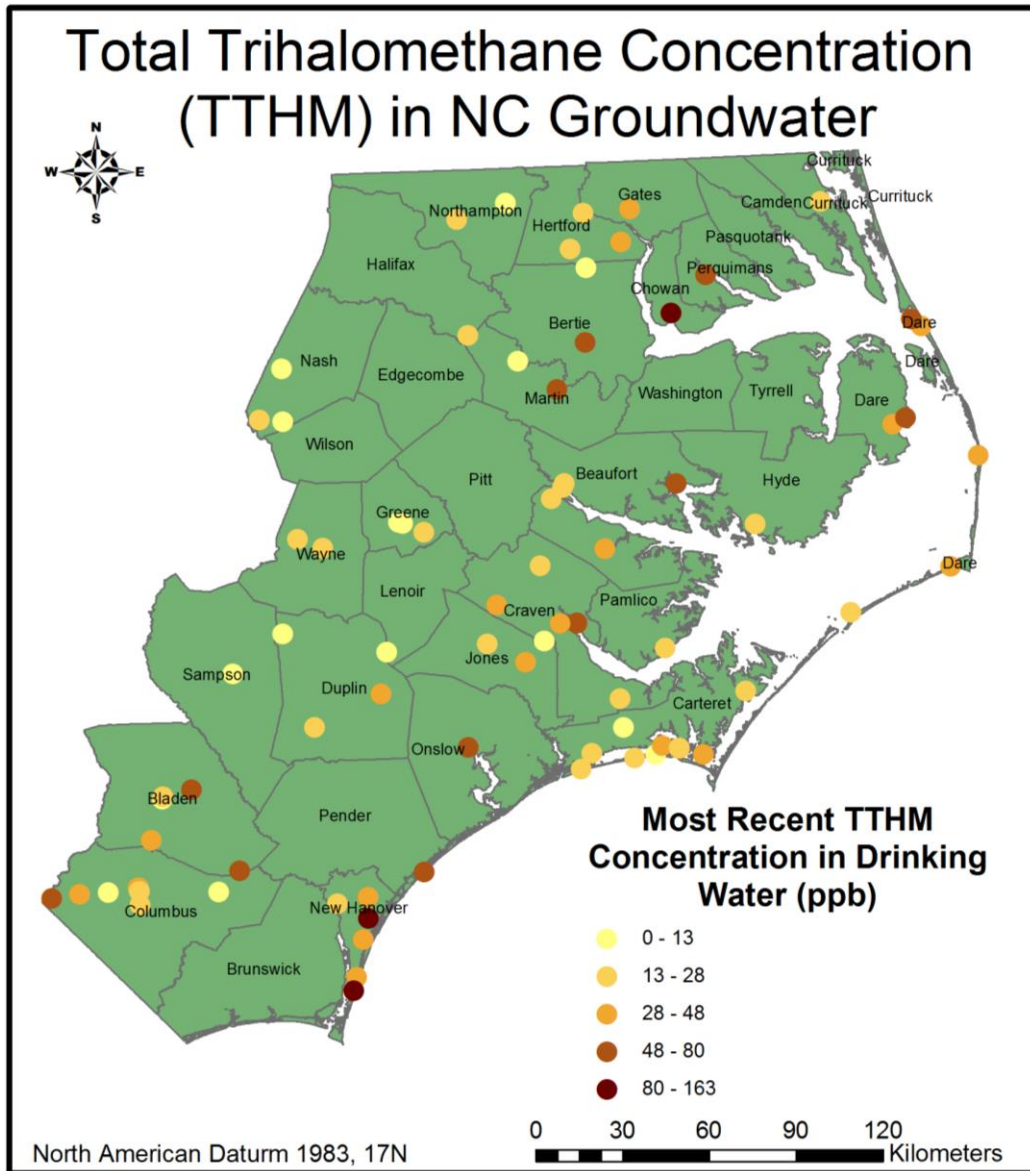


Figure 7: Map of most recently reported TTHM concentrations for 43 Groundwater utilities in Eastern North Carolina.

Two sampling trips were conducted in May and November of 2015 to six and three public water utilities, respectively. Information was collected from each utility on the depth of wells, pumping rates, and distribution. Using a Trimble GPS, data points were collected at the site of each well and monitoring sample and the data was brought back into ArcGIS through ArcPAD for geospatial analysis and spatial characterization of the geochemical results. Samples were collected from an average of 2-4 wells per utility using the Vengosh Lab sampling protocols. A sample of treated drinking water was collected along the distribution system as a

Bromide concentrations in the water samples varied over a much smaller range, however a visible correlation to chloride concentrations can be observed. Again, the three largest sources of bromide were collected from the Yorktown, Cape Fear, Black Creek, and Peedee aquifers. There is, however no Maximum Contaminant Level for bromide in drinking water so this fact does not put any of these samples out of accordance with regulation, however previously discussed studies have shown that increased bromide concentrations do put communities at risk for generating higher levels of trihalomethanes.

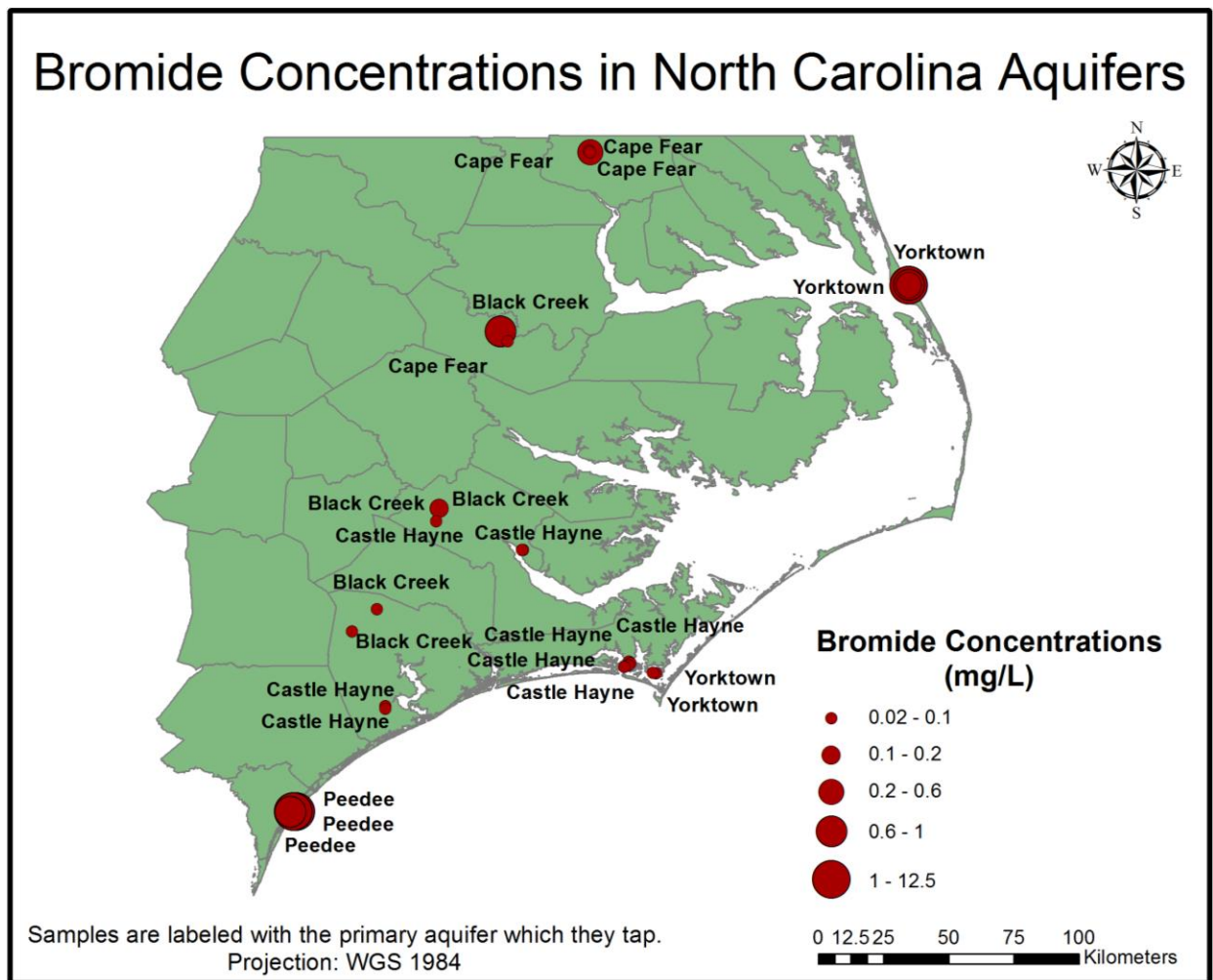


Figure 9: Spatial distribution of bromide ion concentrations in the collected raw groundwater samples.

Concentrations of dissolved organic carbon (DOC), a surrogate for organic matter in drinking water, were also plotted for the collected samples, and is shown in Figure 11. Here there appears to be a spatial trend with proximity to the coast which results in higher concentrations in drinking water, as demonstrated by the black arrows. Again, the samples collected from the Yorktown aquifer which exhibited the highest DOC levels at 79 are those which undergo Reverse Osmosis and the DOC concentrations present in the treated water are much lower. An analysis of the water post Reverse Osmosis revealed DOC concentrations of 0.256 mg/L, and all previous samples for the area contained more than 60 mg/L, suggesting this is an effective treatment for the removal of DOC in source water.

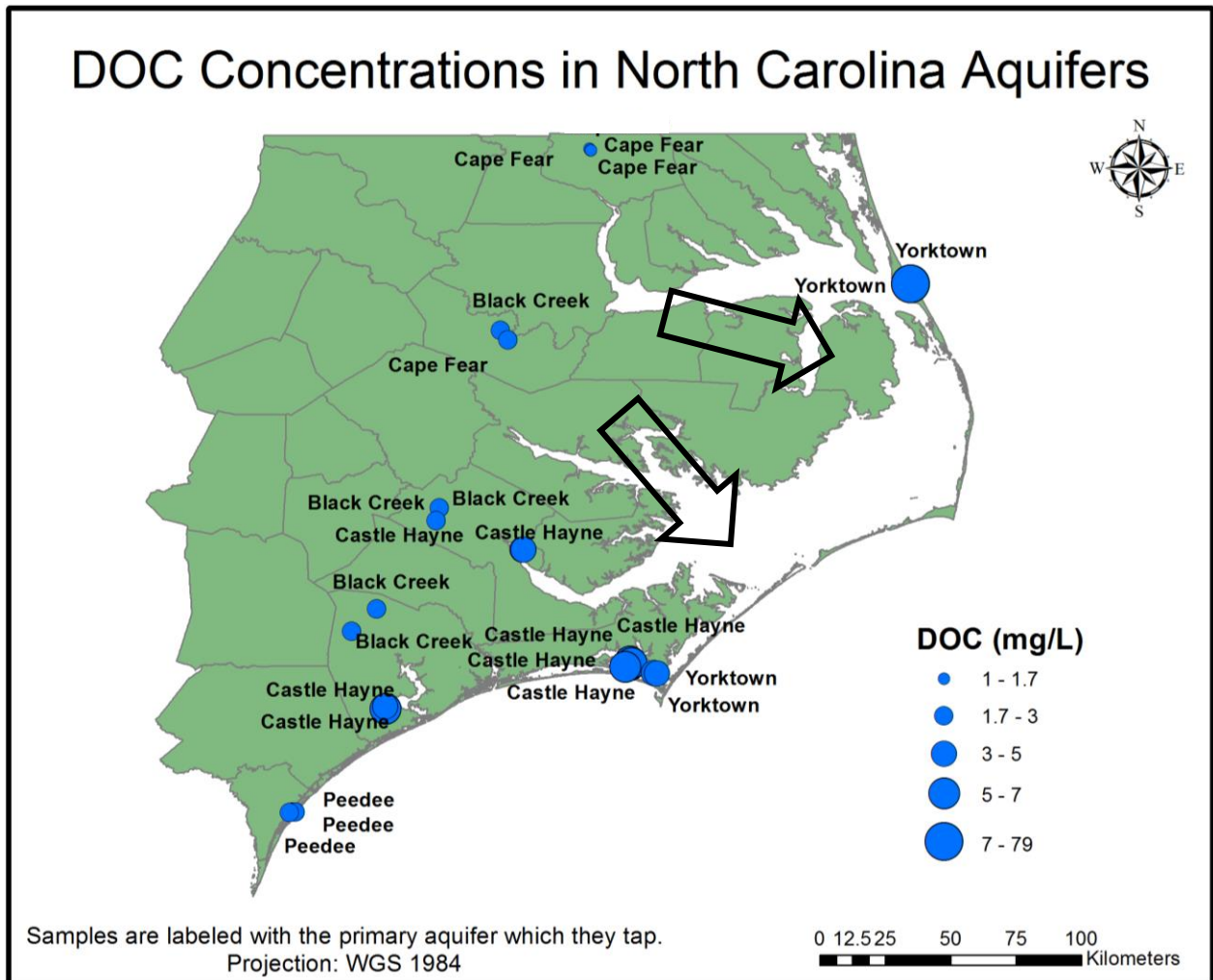


Figure 11: Spatial distribution of dissolved organic carbon concentrations in the collected raw groundwater samples.

Following this sample analysis bromide and chloride concentrations were also examined from several other studies to determine the continuity of these samples with previous research. What was also found was variability in chemical constituents between aquifers and within each aquifer. Figures 12 and 13 show the spatial variability among water samples from the Outer Banks of North Carolina. The southernmost samples are those treated via Reverse Osmosis prior to disinfection and contain high levels of bromide and chloride, up to approximately 25 and 8,000 mg/L, respectively. Even in a relatively small area, however, there is a wide range of concentrations, with no clear spatial trend relating the values. What can be seen from the images is that high chloride levels seem to correspond to high bromide levels across the Skyco samples, and the same appears true for the lower concentrations. These do not appear to be correlated with depth though. According to information provided by the utility, the highest chloride and bromide values, in wells 10, 11, 8, and 7 collectively span a screening depth of approximately 140-220 feet²² which encompasses the range of screening depths for the other wells, including those with very low chloride levels.

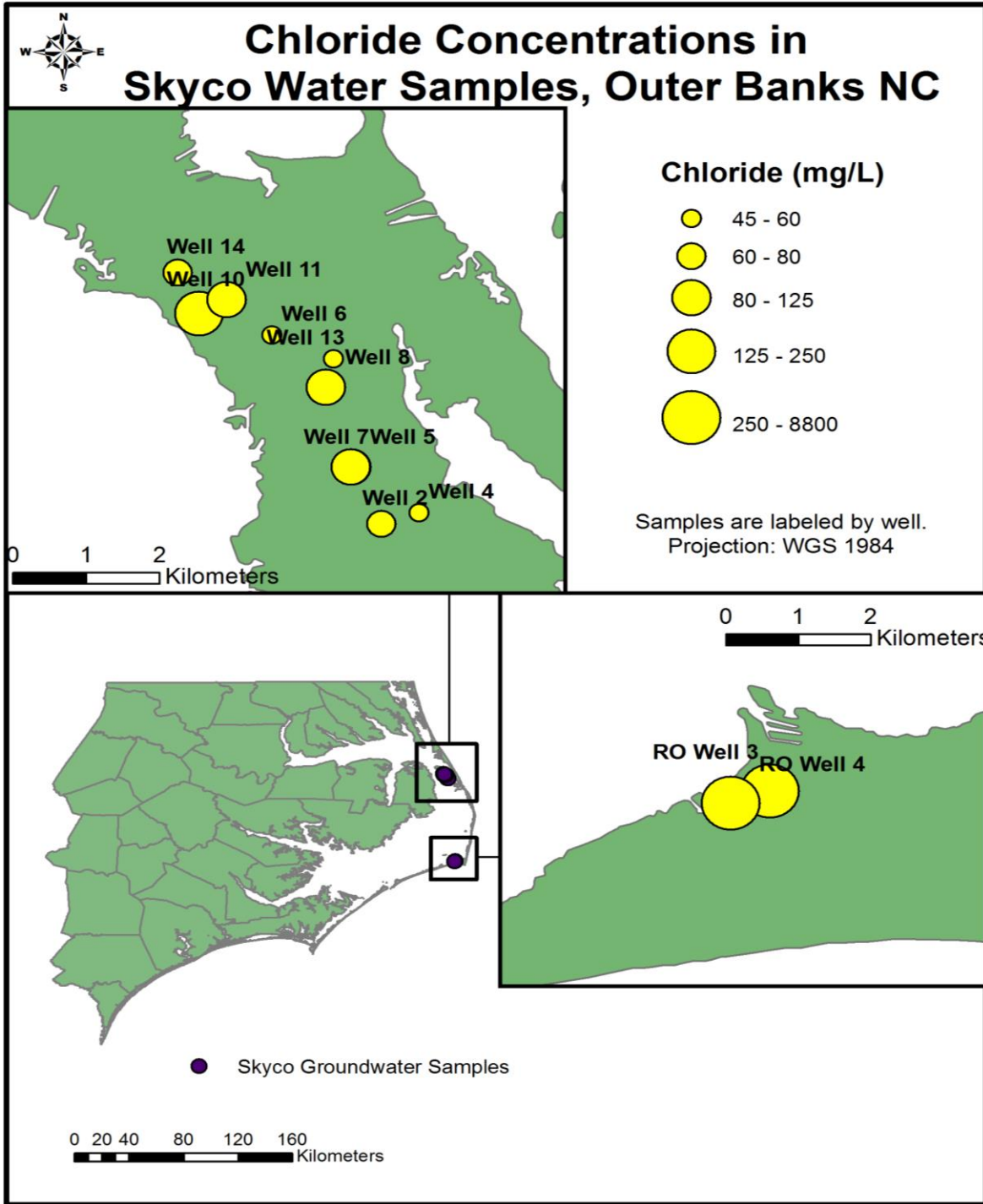


Figure 12: Spatial distribution of chloride ion concentrations in raw water samples collected from the Yorktown Aquifer in Dare County.

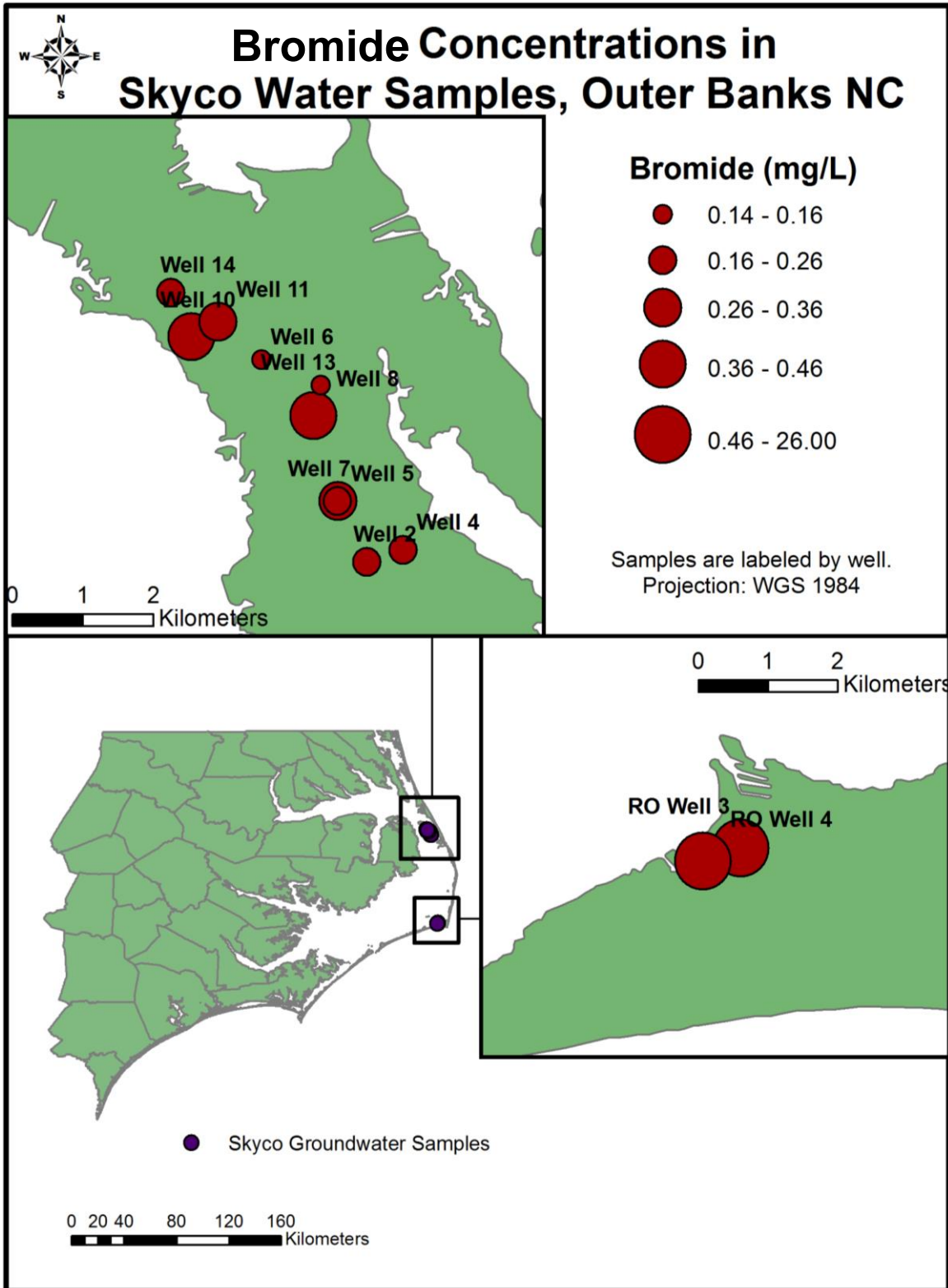


Figure 13: Spatial distribution of bromide ion concentrations in raw water samples collected from the Yorktown Aquifer in Dare County.

The sample data of the Castle Hayne and Peedee aquifers shows spatial variation within aquifers as well, and Figures 14 and 15 also show a correlation between bromide and chloride levels²³. Samples collected from the Peedee aquifer did not show as high levels of chloride and bromide as did those collected from the Castle Hayne, although both exhibited fairly wide ranges. The majority of samples collected from New Hanover and Brunswick demonstrated low levels of chloride and bromide, up to 285 and 0.398 mg/L, respectively²³. Two hot spots for high ion concentrations appear to be at the border between New Hanover and Pender, and at the southern point of Brunswick county, although scientists conducting the study had no explanation for the peak values at the time their report was published²³. With this large variation, however, all collected source samples displayed in Figures 7 and 8 do exhibit bromide and chloride concentrations which are characteristic of previous samples for both of these aquifers.

understandable given that utilities attempting to chlorinate water with high ammonium levels could potentially be inadvertently chloraminating the water, which doesn't produce as many halogenated methanes, but does generate more haloacetic acids. Haloacetic acids were not quantified in our analysis and are not included in this project. This may be the cause for low levels of TTHMs, as well as higher levels of iodinated compounds in the Kill Devil Hills Well #3 sample, given it had the highest concentration of ammonium, 5.41 mg/L.

Electrical conductivity, the ability of a solution to transfer or conduct an electrical current, can be an indicator of dissolved ions in a solution. Conductivity is by no means a precursor, but its method of measurement is simple and could be used as a screening tool by utilities to identify water likely to produce DBPs during disinfection. A mild correlation was found between conductivity and TTHMs ($R^2=0.1668$, P-value=0.0336, F-statistic₂₁₋₁=5.205) as shown in Figure 21c; however in constructing a multiple linear regression using DOC and conductivity as two independent variables, the variation explained by the multiple regression was much higher ($R^2=0.4629$, P-value=0.006), as shown in Figure 22. Both of these measurement methods are relatively simple and efficient. By coupling them, utilities could use this model to more routinely test source water and more easily identify water that is of higher risk for DBP formation. With this information, utilities could implement techniques to prevent or mitigate DBP exceedances, or notify customers of potential DBP exposure.

As these are not the only groundwater utilities in the state of North Carolina, they might not be the only facilities and customers who could be at risk for higher than allowable levels of TTHMs in drinking water. The North Carolina Department of Environmental Quality has been working to generate maps dictating the fresh, salty, and transition zones of the aquifers of the Coastal Plain²⁵. While these are a work in progress and their accuracy has not been independently verified, these maps serve as a starting point for characterizing additional areas of concern, as well as locations for future research.

Beginning with the Yorktown aquifer, there are four utilities which generated anywhere from 48-80 ppb of detected disinfection byproducts in their drinking water. Based on the previous studies of samples collected from the Yorktown, locations on the coast which could well be tapping saline water could be the most in danger of generating over 80 ppb of TTHMs in the future. Of particular concern would be the Belhaven Water System located in Beaufort County which is believed to be underlain by freshwater within the Yorktown aquifer, but the most recent TTHM concentration obtained was above 50 ppb. This salinity map does appear to align with the few samples which were collected, in that those in the freshwater zone do contain less than 250 ppm chloride ions, while samples collected from the transition zone are much more variable with concentrations above and below the 250 ppm threshold. The width of the transition zone, according to the department, corresponds to the dip of the freshwater-saltwater interface, and thus it is possible to encounter water with varying salinities at different depths.

Source Water and Monitoring Samples

Monitoring samples were collected for the purpose of observing the concentrations of chemical constituents pre- and post-disinfection. Not only can they provide information regarding the proportions of each well being used for drinking water at the time, but they also highlight additional treatment in some cases, and inconsistencies in others. Given that our analysis is conducted through the lens of disinfection byproduct formation, the comparison below displays chloride, bromide, iodide, DOC and ammonium concentrations, all prominent chemical factors in DBP formation.

Working down the list, Wrightsville Beach clearly starts with more saline groundwater with chloride levels well above the EPA standard of 250 mg/L in Well #1 and Well #8, but their final consumptive product is well within the chloride standard. The same can be said for the First Craven Sanitary District, where little work is necessary to remove chloride from the system and the monitoring sample concentrations are very similar to both Wells #1 and #2.

Initially taking a sample of source groundwater from Kill Devils Hills (Well #3) proved ineffective because the chloride value was clearly too high and not representative of the water being disinfected. The RO permeate (post-RO, pre-disinfection) showed much lower chloride and bromide concentrations. The monitoring sample however, showed chloride levels higher than the EPA standard, and in both tests, relatively high bromide concentrations compared to samples from some of the other utilities. Considering that not all of Kill Devil Hills wells may have high enough ion concentrations to warrant Reverse Osmosis, this could be the result of mixing between wells prior to entering the distribution system.

The Town of Williamston showed large variation between the two wells we sampled. They collect groundwater from a total of eight wells, so again the high levels could be the result of mixing with other higher chloride groundwater. Regardless, the monitoring sample showed chloride levels much higher than the EPA standard, and aside from the pre-RO sample from Kill Devil Hills, the second highest bromide concentrations of any of the water samples. Harker's Island Sanitary District uses two groundwater wells for their potable water. The monitoring sample shows slightly elevated chloride values compared to either well, but not by an order of magnitude.

Craven County utilizes 10 wells for their drinking water, and the monitoring sample shows that Well #5, or other wells with similar chloride concentrations made up the majority of

the drinking water provided in that sample. The monitoring sample collected on the Onslow Water and Sewer Distribution system tested much higher, yet not over the limit of chloride compared to all of the source groundwater samples collected. This could be a characteristic of the sampling location rather than the raw groundwater. The Town of Beaufort samples show reasonable source and monitoring sample levels of chloride and bromide.

Samples of raw groundwater were collected from each of the wells used by the Gates County Water System. Based on that information, Gates County likely uses a larger percentage of water from Well #1 than either Well #2 or Well #3.

The results of simulated disinfection (in TTHMs, ppb) were also compared to the values obtained by the nine selected drinking water utilities for the most recent year. With the exception of the Town of Beaufort and Harkers Island, all other utilities have more wells than were sampled, and so without specific knowledge of the locations and source water for the portion of the distribution system sampled, it is unclear whether the water which utilities test to record TTHM concentrations ever came from any wells which we sampled. Given the table above there can be a great deal of variation between source water and combined samples. Additionally, the simulated DBP samples were collected as a grab sample, as do water utilities. Water composition and chemical concentrations are extremely varied, and this will vary throughout the aquifer and correspondingly throughout the distribution system.

The table below shows that for each utility, the most recent TTHM value in water quality report is very different, by at least 15 ppb for each well sampled. Only eight of the samples disinfected generated TTHM concentrations less than their previously reported values. The rest were higher, and this can be due to a variety of reasons. In the case of the Skyco source water samples, these are naturally more saline and contain higher amounts of organic matter, hence their water is treated to remove these precursor to form smaller amounts of byproducts in their water. For others, such as Onslow Water and Sewer, which draws water from approximately 37 wells, a small portion if any of the water which we sampled and disinfected may make it to the point in the distribution system which is tested by the utility.

systems. While there is little information based on these collected samples regarding the effectiveness of reducing ions or organic carbon at reducing concentrations of DBPs formed, the statistics speak to a relationship between conductivity and dissolved organic carbon which would suggest that if methods are established to remove these precursors to DBP formation, lower concentrations of TTHMs could be generated as a result.

Uncertainties

There are several uncertainties associated with our research which should be noted in this report. First, high ammonia levels were detected in some of raw samples, up to the point where disinfection simulation via just chlorination was impossible. Adding chlorine to water with high ammonia levels could actually be causing inadvertent chloramination of the water, a different chemical process that produces different DBPs (mainly an increase in haloacetic acids and decrease in trihalomethanes). This could be occurring in some of our samples and could be affecting the TTHM results we see. Unfortunately, quantifying haloacetic acids was out of the scope of our project, but would be necessary for investigating thresholds for these chemical processes.

In our study design, we elected to collect grab samples of water which is constantly flowing. This sampling method only represents one point in time, so we have not accounted for seasonal or production variability in our current research. While this makes comparison to single samples collected by utilities for their water quality reports, as well as our own monitoring samples difficult, we are operating under the same sampling ideology as utilities in determining the geochemical composition of their water supply. Some of the utilities we collected samples from also pre-treat the raw groundwater, whether it be aeration, softening, filtering, or processes to reduce halide and organic matter levels, like reverse osmosis. Our samples are of the raw groundwater and not the pre-treated water to characterize the geochemistry of aquifers and conduct a spatial analysis, and the pre-treated water would contain mixture of all the wells in use.

We also acknowledge a relatively small sample size, and the amount of samples per aquifer was even smaller. To improve the power of our analyses, additional sampling is needed.

Conclusion

15 out of 26 collected samples were found to exceed the EPA MCL of 80 ppb for Total trihalomethane Concentrations. Although this is just a snapshot in time, it is still alarming that these chemicals are so prevalent in the North Carolina Coastal Plain. Because the Coastal Plain extends most of the Eastern seaboard, it is possible that groundwater-dependent coastal communities within a broader range could be experiencing higher levels of DBP formation and subsequent exposure.

Based on our data, halide concentrations in groundwater samples are most likely a result of saltwater intrusion, as the Cl/Br plots show an approximate following to the seawater intrusion line. Although different aquifers could be experiencing salinization at different rates, this finding is important because projected sea level rise and increased water usage will only quicken salinization of these aquifers. Increasing concentrations of halides, especially bromide and iodide which are generally associated with seawater in higher concentrations, may increase potential DBP formation. These results suggest that the EPA may need to establish MCLs for DBP precursors as part of a public health effort to reduce population-wide exposures of potential carcinogens.

It can also be concluded that water treatment should be both aquifer and location specific, due to the intra-aquifer chemical variability. Some utilities have already implemented pre-treatment techniques to prevent DBP formation or, in Dare County's case, to mitigate DBP formation. Dare County, whose raw wells had some of the highest halide and organic matter concentrations, has an extensive system of both Reverse Osmosis and Ion Exchange to pre-treat water before disinfection. Dare County draws from the Yorktown aquifer, which in that specific area, is very saline. However, processes like these would not be necessary at other utilities that are not dealing with as high of levels as Dare County. Possibly the most important finding is the relationship between conductivity, dissolved organic carbon, and TTHM formation. Conductivity and DOC measurement methods are relatively cheap and efficient. By establishing a threshold for these parameters, utilities could potentially use these methods in concert with one another to identify raw water that is likely to exceed the MCL once disinfected. Water could be tested via this method more frequently than DBPs are tested for, and could contribute to the prevention of so many exceedances.

Acknowledgements

We would like to thank our advisor, Dr. Avner Vengosh for his guidance and advice throughout this research project, as well as Dr. William Mitch for providing disinfection simulation of collected water samples and providing insight into data analysis. Laboratory equipment and geochemical sampling was conducted at Duke University, with the help of Gary Dwyer, Jennifer Harkness, Nancy Lauer, and Andrew Kondash. Additionally, we thank the water utility directors and staff in North Carolina which we spoke to or who allowed us to collect samples.

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- ²⁷VanBriesen, J.M. (2013). Potential Drinking Water Effects of Bromide Discharges from Coal-Fired Electric Power Plants. <https://www3.epa.gov/region1/npdes/merrimackstation/pdfs/Comments2RevisedDraftPermit/VanBriesenReport.pdf>

Appendix D. R code for statistical analyses

```
data <- read.csv("thmeval.csv", header=T)
attach(data)
data

par(mfrow=c(1,2))
mod1 <-lm(total~CL, data=data)
summary(mod1)
plot(CL,total, xlab="Chloride, ppm", ylab="TTHM, ppb", main="Relationship of
Chloride \nand Total Trihalomethanes", col="black", pch=1, cex=1.2)
coef1 <- coefficients(mod1)
x <- seq(min(CL[-c(1,3)]), max(CL[-c(1,3)]))
curve(coef1[1]+coef1[2]*x, add=TRUE, col="blue", lwd=2.7)
abline(h=80, col="red", lty=2)
legend(500,25, col=c("red", "green"), c("EPA MCL for TTHM", "EPA MCL for
Chloride"), lty=2, cex=0.8)
abline(v=250, col="green", lty=2)

mod1 <-lm(totC~CL, data=data)
summary(mod1)
plot(CL,totC, xlab="Chloride, ppm", ylab="Chlorinated Haloforms, ppb",
main="Relationship of Chloride and \nTotal Chlorinated Haloforms",
col="black", pch=1, cex=1.2)
coef1 <- coefficients(mod1)
x <- seq(min(CL), max(CL))
curve(coef1[1]+coef1[2]*x, add=TRUE, col="blue", lwd=2.7)

mod1 <-lm(total~ratio, data=data)
summary(mod1)
plot(ratio,total, xlab="Ratio, ppm", ylab="TTHM, ppb", main="Relationship of
Chloride \nand Total Trihalomethanes", col="black", pch=1, cex=1.2)
coef1 <- coefficients(mod1)
x <- seq(min(ratio), max(ratio))
```



```
mod1 <-lm(total~CON, data=data5, ma.omit=T)

summary(mod1)

plot(CON, total, xlab="Conductivity, uS", ylab= "TTHM, ppb",
main="Relationship of Conductivity and \nTotal Trihalomethanes", col="black",
pch=1, cex=1.2)

coef1 <- coefficients(mod1)

x <- seq(min(CON), max(CON))

curve(coef1[1]+coef1[2]*x, add=TRUE, col="blue", lwd=2.7)

abline(h=80, col="red", lty=2)

legend("bottomright", col=c("red"), c("EPA MCL for TTHM"), lty=2, cex=0.8)
```



```
arcpy.Select_analysis(aquifers, TTHM, "\"F_TTHM__mo\" >30")
```

```
# Process: Final Site Selection
```

```
arcpy.Select_analysis(TTHM, Nine_Uilities, "\"Water_Syst\" = 'BEAUFORT, TOWN OF' OR  
\"Water_Syst\" = 'CRAVEN COUNTY WATER SYSTEM' OR \"Water_Syst\" = 'DARE  
COUNTY WATER SYSTEM' OR \"Water_Syst\" = 'FIRST CRAVEN SANITARY DISTRICT'  
OR \"Water_Syst\" = 'GATES COUNTY WATER SYSTEM' OR \"Water_Syst\" = 'HARKERS  
ISLAND SANITARY DIST' OR \"Water_Syst\" = 'ONSLOW WTR AND SEWER  
AUTHORITY' OR \"Water_Syst\" = 'WILLIAMSTON, TOWN OF' OR \"Water_Syst\" =  
'WRIGHTSVILLE BEACH WATER SYST'")
```